FIRST NATIONAL CONFERENCE ON ELECTRON PROBE MICROANALYSIS

CENTER OF ADULT EDUCATION
UNIVERSITY OF MARYLAND

COLLEGE PARK, MARYLAND
4 - 6 MAY, 1966

FIRST NATIONAL CONFERENCE ON ELECTRON PROBE MICROANALYSIS

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ABSTRACTS

1

ANDERSEN, C. A. - The Quality of X-Ray Microanalysis in the Ultra-Soft X-Ray Region.

The quality of a microanalysis by x-ray means is determined by the degree of spatial resolution attained, the sensitivity of detection, the precision of the measurement, and the accuracy of the measurement. These parameters are discussed in their relationship to the ultra-soft x-ray region.

Spatial resolution is determined by the volume of the sample which through excitation by the primary electron beam contributes to the analysis. The size of the excited volume is a function of the range of the primary electrons, and hence their accelerating potential, and the excitation potential of the particular characteristic x-ray lines utilized for the analysis. The inter-relationships of these variables produce the general result that the smallest excited volumes and therefore the best spatial resolution can be attained by employing low accelerating potentials.

Sensitivity of detection is commonly considered in two categories. The first, the weight fraction or relative detection limit, describes the smallest weight fraction of the analytical element detectable in the sample irrespective of the volume which must be excited to achieve this limit. The second, the absolute detection limit, gives the smallest number of atoms, which may be expressed in grams, necessary for the analysis. The first is

dependent on the integrated intensity received from the analytical line and its associated background and is therefore a function of the x-ray line utilized, the accelerating potential of the primary electron beam, and time. The second is dependent on the weight fraction detection limit and the volume excited and hence being analyzed. The ideal in microanalysis is to detect as few atoms of an element as possible in as small a volume as possible. To accom-polish this goal the various x-ray lines available for analysis are studied with regard to their relative intensities, associated backgrounds, and dependences on accelerating potential. Very often the use of low accelerating potentials and lines of the ultra-soft spectrum provide the highest sensitivities of detection attainable.

The precision of an analysis describes the limits of reliability which can be assigned to a reported value in consideration of the errors involved in the measurement itself. Included in these errors are such things as instrumental drift, x-ray statistics, differences in surface contamination, and differences in unseen sub-surface composition. The relative precision of analysis from point to point is very important in microanalysis and usually very good with the electron probe. The use of low accelerating potentials will improve this precision with respect to differences in sub-surface composition while affecting it adversely with respect to differences in surface contamination and coatings.

The accuracy of the measurement is a description of how close the results of the quantitative analysis are to the true composition. Accuracy in electron probe microanalysis is, therefore, dependent on the validity of the correction procedure employed, the quality of the reference standards utilized, and the imposed instrumental analysis conditions. Since a complete understanding of the correction theory is lacking the greatest accuracy can be obtained by reducing the magnitude of the various corrections and using standards closely resembling the samples under study. In the ultra-soft x-ray region the major correction, absorption, can be reduced by lowering the accelerating potential of the primary electron beam. The minor corrections due to differences in atomic number are probably increased and those due to fluorescence are decreased. Suitable standards are discussed with special emphasis on those required for biological analyses.

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2

BAUN, W. L. and FISCHER, D. W. - Effects of Alloying on K and L X-Ray Emission Spectra.

Large changes in x-ray emission spectra are observed between some

pure elements and those elements combined with other elements to form a compound or alloy. In this paper AlK and NiL data from Al-Ni alloys are emphasized and compared to other binary systems such as Al-Mg, Al-Cu, Al-Ag, and Al-Zr and to several ternary systems. Measurements of band and line shifts and intensity and shape changes are reported. Most data were obtained using primary electron excitation of macro areas, but for a number of two phase alloy compositions, microbeam probe methods were used to determine spectral differences between the phases. Theoretical considerations and practical uses of these spectral changes are illustrated.

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3

BEAMAN, D. R. - The Evaluation of the Correction Procedures Used in Electron Probe Microanalysis with Emphasis on the Atomic Number Interval 12 to 33.

The aim of this investigation was to determine if any of the many available correction techniques could be satisfactorily utilized in correcting probe data obtained in the low atomic number systems (Mg, Al) frequently encountered at Dow, where due to large absorption effects any quantitative work had heretofore only been possible when using calibration standards. Absorption and characteristic fluorescence correction techniques were applied to a large number of alloys, and the precision and accuracy of each technique were evaluated with respect to atomic number interval (12 to 14, 22 to 33, and 12 to 33) and probe ratio ($k > 0.1$ and $k < 0.1$). Atomic number corrections were made and some procedures were found to be detrimental to the results obtained in systems where small atomic number effects were expected.

All of the published absorption and characteristic fluorescence correction procedures and modifications of some have been evaluated. It was found that while a large number of correction procedures are available only a few gave satisfactory accuracy and precision. By careful selection of the correction procedure used, it is possible to remove over 90% of the measured probe error with good accuracy and precision ($\pm$1-4%).

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BOROVSKII, I. B., and RYDNIK, V. I. - The Theory of Quantitative Local X-Ray Spectral Analysis.

This paper proposes a method of introducing a correction to the results of local x-ray spectral analysis based on the use of the excitation function $\psi(x)$ of the characteristic x-radiation as a function of depth in the sample. In the case of x-ray excitation by electron bombardment, it is assumed that:

$$\psi(x) \sim \int_{E_0}^{E_i} \left\{ \frac{g(x,E)}{\cos\varphi_1(x)} + \frac{G(x,E)}{\cos\varphi_2(x)} \right\} \sigma(E,E_i)\, dE \quad \ldots\ldots (1)$$

where g and G represent the energy distribution of forward scattered ($0 \leq \varphi_1 \leq \pi/2$) and back scattered ($\pi/2 \leq \varphi_2 \leq \pi$) electrons, $E/E_0 = \xi$, $E_i/E_0 = \xi_i$, E_0 and E_i represent the initial electron energy and the excitation potential of an analyzed series of characteristic x-ray spectral lines $x = x/X$, X-represents the characteristic radiation parameter in the law of electron beam attenuation given in the paper by Makhov and Dupuoy (1, 2).

It is shown that g may be determined according to Makhov (1), if it is postulated that the change in energy of any group of non-parallel electron beams at any depth in the sample is expressed by the ratio $\xi_i^n = 1 - \frac{x}{x_i}$, where ξ_i - is the energy of the selected group, ... x_i is the mean free path limit of this group. For calculating the energy distribution G an original model of back-scattered electrons is developed,.. $\overline{\cos\varphi_1}$ .... is determined according to the diffusion theory of electrons (3), $\overline{\cos\varphi_2}$ is calculated for single elastically scattered electrons. An ionization cross section is given by Green and Cosslett (4).

Calculating with the help of (1), $\psi(x)$ is found to be in good agreement with the measurement for copper by Castaing and Descamps (5) in all regions. Estimation of x_{max} for ψ_{max} and $\psi(0)$ for other elements also is frequently very close to the experimental results (5).

The proposed approximation for $\psi(x)$ is given by:

$$\psi(x) \sim \frac{\ln\beta}{\beta} \exp\left\{ - \frac{\rho x}{\alpha E_i^n(\beta^n - 1)} \right\}, \quad \ldots\ldots (2)$$

where $E_0/E_i = \beta$. The derivation of the theoretical expression for the functions $I(\beta)$ and $I(\mu \operatorname{cosec}\theta)$ where:

$$I = \int_0^\infty \psi(x)\, e^{-\mu x \operatorname{cosec}\theta}\, dx \quad \ldots\ldots\ldots\ldots (3)$$

represents the x-ray intensity emitted by the sample, which agrees with reported experimental measurements (6, 7) in a wide range

of E_o values and for elements with atomic numbers Z down to the very light elements.

On the basis of the ratio obtained, the expression for simultaneous correction for atomic number and absorption is given. Also, it is pointed out how fluorescence corrections must be made more precise. Equations are derived for the introduction of corrections used for calculation of concentrations according to the important ratio of intensities of samples and pure element standards, particularly, for the system Fe-Cr, investigated by Colby and Conley (8). In all cases, quite satisfactory agreement with the experimental values was obtained.

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2. G. Dupuoy et. al., C. R. 258, 3655, (1964); 260, 6055 (1965).
3. C. Blanchard, U. Fane, Phy. Rev. 82, 767 (1951).
4. M. Green, V. Cosslett, Proc. Phys. Soc. 81, 1206, (1961).
5. R. Castaing, J, Descamps, J., Phys. Rad. 16, 304, (1955).
6. M. Green, X-Ray Optics and Microanalysis, N. Y., (1963) p. 361.
7. A. Campbell, Proc. Roy. Soc. A274, 319 (1963).
8. J. Colby, D. Conley, NLCO Rep. #960, (1965).

(Translation by Cynthia W. Mead; Drs. Borovskii and Rydnik did not have the opportunity to see it, therefore, their original in Russian follows):

И.Б.БОРОВСКИЙ и В.И.РЫДНИК

К теории количественного локального рентгеноспектрального анализа

В работе предложен метод введения поправок к результатам локального рентгеноспектрального анализа, основанный на использовании функции возбуждения $\psi(x)$ характеристического излучения в зависимости от глубины в образце. При возбуждении излучения электронным ударом принимается, что:

$$\psi(x) \sim \int_{E_0}^{E_i} \left\{ \frac{g(x,E)}{\cos\varphi_1(x)} + \frac{G(x,E)}{\cos\varphi_2(x)} \right\} \sigma(E,E_i)\, dE, \qquad (I)$$

где g и G - энергетические распределения рассеянных вперед ($0 \leq \varphi_1 \leq \pi/2$) и назад ($\pi/2 \leq \varphi_2 \leq \pi$) электронов,

$E/E_0 = \xi$, $E_i/E_0 = \xi_i$, E_0 и E_i – начальная энергия электронов и энергия возбуждения анализирумной серии характеристического спектра, $\chi = x/X$, X – характерный параметр в законе ослабления электронного пучка в веществе по Махову – Дюпюи [1,2].

Показано, что g можно определить по Махову [1], если постулировать, что изменение энергии любой группы непараллельного пучка электронов на любой глубине вещества выражается соотношением $\xi_i^n = 1 - \frac{\chi}{\chi_i}$, где ξ_i – энергия выбранной группы, χ_i – предельный пробег этой группы. Для нахождения распределения G развита оригинальная модель обратного рассеяния электронов. $\overline{\cos\varphi_1}$ определяется согласно теории диффузии электронов [3], $\overline{\cos\varphi_2}$ рассчитывается для однократного упругого рассеяния электронов. Сечение возбуждения излучения берется по Грину и Косслетту [4].

Вычисленная с помощью (1) $\psi(x)$ находится в хорошем согласии с измеренной для меди Кастеном и Дешаном [5] во всей области. Оценки $x_{макс}$ для $\psi_{макс}$ и $\psi(0)$ для других элементов также численно очень близки к результатам [5].

Предложена аппроксимация для $\psi(x)$ в виде:

$$\psi(x) \sim \frac{\ln\beta}{\beta} \exp\left\{-\frac{\rho x}{\alpha E_i^n(\beta^n - 1)}\right\}, \qquad (2)$$

где $E_0/E_i = \beta$. Полученные теоретически выражения для зависимостей $I(\beta)$ и $I(\mu\,\mathrm{Cosec}\,\theta)$, где

$$I = \int_0^\infty \psi(x) e^{-\mu x\,\mathrm{Cosec}\,\theta}\,dx \qquad (3)$$

– интенсивность излучения, выходящая из образца, находятся в отличном согласии с результатами измерений [6,7] в широком диапазоне E_0 и атомных номеров Z вплоть до самых легких элементов.

На основе полученных соотношений даются выражения для одновременной поправки на атомный номер и на поглощение. Также показывается, каким образом должна быть уточнена поправка на флуоресценцию. Полученные формулы для введения поправок использованы для вычисления концентраций по значениям отношения интенсивностей от образцов и стандартов из чистых элементов, в частности, для системы Fe - Cr, исследованной Колби и Конли [8]. Во всех случаях получено вполне удовлетворительное согласие с опытом.

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2. G.Dupuoy et al,C.R. 258,3655 (1964); 260, 6055 (1965).

3. C. Blanchard, U. Fano, Phys. Rev. 82, 767 (1951).

4. M.Green, V. Cosslett, Proc.Phys.Soc. 81, 1206 (1961).

5. R.Castaing, J.Descamps, J.Phys.Rad. 16, 304 (1955).

6. M.Green, X-Ray Optics and Microanalysis,N.-Y.,1963,p.361.

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5

BIRKS, L. S., GILFRICH, J. V., AND YAKOWITZ, H. - Report of the Washington Electron Probe Users' Group.

The Washington Electron Probe Users' Group which consists of approximately twenty persons representing some ten laboratories in the area was established in December, 1964. This group meets monthly for informal exchange of information concerning current research practices and techniques. Instruments of three commer-

cial firms as well as laboratory constructed instruments are represented. It became apparent to the group that there were problems of importance which could not be resolved through discussion alone.

In order to clarify these problems, several systems of alloys and minerals were carefully selected for collective study and comparison. Wherever possible, these systems were chosen so that absorption, fluorescence, and atomic number factors could be individually evaluated. For example, in the iron-nickel system, only an absorption conversion is required for nickel while a relatively large fluorescence correction is necessary for the iron. In each of these tests, relative x-ray intensity data taken from instruments of the same manufacturer were compared in order to determine variations in the measurement process; in virtually all cases, agreement was excellent. Thus, it was deemed possible to evaluate conversion procedures for their relative merits. In cases where only absorption is important, the major source of variability has been the x-ray mass absorption coefficient uncertainty rather than the conversion procedure. However, when fluorescence corrections are required, the available conversion procedures seem to lead to greater variability; and work is continuing on this evaluation. The need for an atomic number conversion has been established, but the variability associated with the procedures described in the literature leads to even greater uncertainty than the fluorescence conversion; this may be due to the fact that no completely acceptable theoretical basis for the atomic number conversion has yet been proposed. In all of this work, an interesting observation has been that addition of the determined concentrations to 100% is not a sufficient criterion for judging the correctness of the conversion procedure.

As a result of the experiences of the Washington Electron Probe Users' Group, advantages to individual laboratories from such group participation can and will be pointed out and suggestions given for the formation of electron probe users' groups in other sections of the country.

6

BROWN, J. D. - Study of Secondary Fluorescence Using a Sandwich Sample Technique.

Measurement of the distribution Ø(z) of the direct production of X-rays by an electron beam as a function of depth in the sample was first described by Castaing and Descamps. A sandwich sample was

used in which a thin layer of one element, the tracer, was deposited on a block of a second element, then covered with successively thicker layers of the second element. The tracer element was chosen so as to be close in atomic number to the base element, yet not subject to excitation by the characteristic lines of the base element. In this way measurement of the X-ray intensity from the tracer element yielded the distribution of primary X-rays as a function of depth in the sample.

The distribution of secondary radiation can be determined using the same sandwich sample technique. In this case two samples are necessary, one in which the tracer is not subject to excitation due to absorption of radiation of the base element, and one in which the tracer is subject to excitation. Such a pair of samples are represented by tracers of zinc and cobalt in copper. This difference between the two measured ϕ (pz) curves, represents the distribution in depth for a trace concentration of cobalt in a copper matrix. Only a minor correction is required for the difference in excitation potential for the ZnK and CoK lines. By using L lines, a more subtle determination of the secondary distribution can be obtained. By selecting a heavy element as tracer such that the L_{III} and L_{II} edges are of lesser and greater energy than the energy of the Kα line of the base, selective excitation can occur in which the Lα_1 line intensity contains a contribution due to secondary fluorescence but the Lβ_1 line intensity does not. Then by measuring $\phi(\rho z)$ for the two spectral lines in one sample, the distribution of secondary radiation can be obtained.

Results of measurements of selected tracers in a copper matrix at electron accelerating voltages from 10-30 Kev have been obtained. The distributions of secondary radiation are compared to theoretical predictions.

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7

COLBY, J. W., WISE, W. N., and CONLEY, D. K., - Microprobe Analysis By Means Of Target Current Measurements.

In the microprobe analyzer, a portion of the high energy electrons impinging on the surface are backscattered from the sample and re-emitted at high energy levels. Low energy (less than 50 ev) or secondary electrons are also emitted. Both the electron back-

scatter yield and the secondary electron yield are related to the mean atomic number of the target material, and hence may be used to provide information about the target composition. Unfortunately, however, the secondary electron yield is very sensitive to the surface condition of the specimen and various instrument parameters, and consequently complicates the otherwise simple linear relationship between sample composition and electron backscatter yield.

It is shown that the effects due to secondary electrons can be minimized by biasing the sample, and that good results can be obtained in the analysis of binary systems. The limitations of the method are discussed, backscatter yields are determined, and the utility of the method are discussed.

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8

COX, RONALD H., and SMITH, JAMES P. - Electron Probe Microanalysis of Ohmic Contacts to GaAs.

Ohmic contacts to semiconductors are of major concern in the fabrication of semiconductor devices. This is particularly true in the case of GaAs since its technology is at an earlier stage of development as compared to Ge or Si. An important requirement in making ohmic contacts to any semiconductor is that the contact must meet metallurgical as well as electrical requirements. The development of new contact materials often requires the use of ternary alloys and the phase diagrams of these alloys are generally unknown. The phase equilibria may be further complicated if the GaAs reacts with the contacting alloy. Because of these factors, the creation of new contact materials can be difficult if only metallographic methods are used. The electron probe microanalyzer is particularly applicable to such a program due to its ability to detect the relative amounts of the constituent elements. Coupled with metallographic methods and simple electrical measurements, the task of finding new contact materials to semiconductors is greatly simplified. A microprobe study performed on ternary alloy contacts to GaAs is given as an example of the technique. Metallographic methods were used to supplement the microprobe data. Both melt-grown and epitaxial (100) oriented GaAs were contacted. The GaAs slices were coated with 3000A of SiO_2, small area windows (4-32 mils^2) were cut in the SiO_2, and the metal was thermally evaporated on to the substrates. The metallized slices were alloyed at 500 - 600° C.

HF was used to remove the SiO_2 layer and excess metal. Identification of the various phases was accomplished by electron probe quantitative analysis. The surface distribution of the elements was mapped by X-ray intensity topographs. Homogeneity of the dopant distribution was studied by using concentration profiles through the contacts. Angle-lapped sections were examined to determine the nature of the metal-GaAs interface. Sections of Au bonds to the contacts were also studied. During the processing of the contacts, microprobe examinations were used to monitor the effects of the various fabrication steps. A particularly important consideration was the behavior of the contacts toward the reagents employed, especially HF. (This work supported in part by the U. S. Air Force Avionics Laboratory).

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9

DAVIDSON, E. and NEUHAUS, H. - Sample Image Displays for Qualitative Microprobe Analysis.

The qualitative and quantitative determinations with an electron microprobe depend upon the quality and versatility of the visual optical system, the resolution and efficiency of the electron optics, and the detection capability of the x-ray spectrometers. The additional ability to scan an unknown sample with the electron beam in synchronization with the sweep on a cathode ray tube (CRT) has proved to be an invaluable aid to the analyst in the rapid survey of sample structure and composition. Semiquantitative information can be quickly obtained from electron and X-ray images derived in that manner.

In order to study the topography and surface effects of specimens even more readily, it has been shown that images formed by the collection of secondary or low energy (0 to 50 EV) electrons can be used in a complimentary fashion with absorbed and back-scattered (high energy) electron images. Since a small change in surface potential causes a relatively large change in the trajectory of the secondary electrons, it is possible to observe voltage contrast in the evaluation of semiconducter devices and integrated circuits. The addition of a secondary electron detection system to an experimental model of an Electron Microprobe X-Ray Analyzer has been investigated.

Several important changes to the original design are necessary to retain the major features of the instrument, i.e., normal electron

beam incidence, high X-ray emergence angle, and efficiency of the X-ray spectrometers. A difference magnetic objective lens is being evaluated to permit the appropriate placement of an energy selector, scintillator, and detector for the low energy electrons. This change in objective lens design also affords a greater latitude in sample handling.

Examples of electron images of organic substances and micro-electronic devices have been obtained at low sample currents and low excitation voltages.

The experiments prove the feasibility of expanding the analytical capability of the electron microprobe considerably beyond the original design concepts.

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10

DORSEY, JOHN R. - Scanning Electron Probe Measurement of Magnetic Fields.

A preliminary investigation has shown that it is possible to detect magnetic field strengths of less than 100 gauss at the surface of magnetic recording tape using the secondary emission generated by a scanning electron beam of 10 microns in diameter. Two detector surfaces of equal area are located on opposite sides of the field vector so that the signal due to backscatter and secondary emission current collected by one surface may be subtracted from that collected by the other surface. This differential signal should be zero in the absence of field for a smooth specimen surface normal to the incident beam since the secondary emission is spatially distributed approximately as the cosine of the angle about the normal to the specimum surface. The secondary electrons, because of their low energy (on the order of 5 ev), will be deflected by a surface field such that the increase in the current collected by one detector surface is approximately equal to the decrease in the current collected by the other surface. Therefore, the differential signal is twice the change in the signal from either detector surface and the background signal is zero under ideal conditions.

The scanning electron probe output from magnetic tape recordings of periodic signals has been analyzed and experimental data has been obtained which demonstrates the feasibility of this technique. The data is in the form of a conventional amplitude

modulated display of the scanning electron probe image as well as a display having the appearance of a perspective view of a 3 dimensional surface where quantitative information as a function of 2 dimensions of position is available.

One area of improvement in this technique would be in the deposition of a better specimen surface, namely a smooth, high secondary yield but low backscatter yield, non-magnetic, conducting thin film of thickness considerably less than the wavelength of the recording being analyzed. Another, and potentially a more significant area of improvement would be in the development of a multiplier type of detector with a large collection aperture that would not introduce fields in the vicinity of the specimen large enough to significantly distort the spatial distribution of secondary emission. The input resistor noise of the field effect amplifier used in the present detector system limits the minimum detectable signal current to about 10^{-10} amp at a bandwidth of 50 kcps.

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11

DUERR, J. S., and McCALL, J. L. - Practical Considerations of Back-Reflection Kossel Diffraction.

The ability to perform Kossel-line diffraction with the electron probe microanalyzer has permitted precise measurements of crystal orientation and lattice parameter in micron-sized volumes. This method of micro-diffraction, either by transmission or by back-reflection, is slowly developing into an extremely useful laboratory tool for routine analysis. The back-reflection configuration for Kossel diffraction is particularly well suited for this type of analysis because standard microprobe samples may be used, exposure times are short, and phases can be analyzed which are only slightly larger than the crystal volume excited by the electron beam. Back-reflection patterns, however, have been found to have poorer quality than those produced by transmission.

The quality of back-reflection Kossel-line patterns is dependent on a number of factors, including the type of film and film holder, the condition of the sample surface, and the selection of exposure parameters. These factors have been investigated for Kossel diffraction with the A.R.L. microprobe. The low-speed high-contrast Kodak Type M X-ray film used with Kodak DK-50 developing solution has been found to give good results. The film holder for back-reflection

must have a conducting filter mounted between the film and specimen to capture the back-scattered electrons. Aluminum foil has been used because it makes a light-tight film holder, but a much more durable filter is 20 mil cellulose acetate sheet coated with a 100 Å layer of vapor-deposited carbon.

Since the back-reflection Kossel-line pattern is formed just beneath the surface, careful sample preparation is required. The surface must be flat and free of disturbance. In all cases, a rough grind through 600-grit abrasive followed by a short electro-polish or a 1.0μ diamond mechanical polish has resulted in very diffuse Kossel lines or no lines at all. For most materials, the best patterns have been obtained from surfaces prepared with a careful mechanical polish through 0.03μ alumina plus a short electro-polish.

For a particular material, variation of any of the three important exposure parameters --accelerating voltage, sample current, and exposure time--were found to produce no significant change in pattern quality as long as the product of these parameters remained constant. Some examples of conditions used are 30 kv, 1.0μA, and 180 sec for iron, and 45 kv, 3.0μ A, and 60 sec for molybdenum.

Procedures to shorten the time-consuming task of analyzing the Kossel-line pattern, once it is formed, have been evaluated. Comparison to standard stereographic projections is not satisfactory for routine laboratory analysis because a standard projection must be constructed for each lattice structure and wavelength used. A more practical method--when analyzing many different types of crystals--is to compare calculated Kossel-line radii and interplanar angles to those found on the pattern.

The Kossel diffraction method has been used successfully to study crystallographic relationships such as those between adjacent grains, phases, or a precipitate and its matrix. The method has also been used to study variations in lattice parameter over small distances.

The orientation relationship of copper grains and their annealing twins has been investigated. The twinning plane was found to lie within 1° of the (111) plane--the known twinning plane in copper--in both the grain and the twin.

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12

DUNCUMB, P., and MELFORD, D. A. - A Simple Correction Procedure For Ultra-Soft X-Ray Microanalysis.

Some of the special considerations in extending the theory of quantitative analysis to the 10-100 Å X-Ray region were described at the 4th International Conference on X-Ray Optics and Microanalysis, Paris, 1965. In general, mass absorption coefficients are greatly increased in this region, with the result that the penetrating power of the incident electrons is often greater than that of the emitted X-rays. This is particularly the case at high beam voltages (20-30KV), when only the radiation from a thin surface layer of the sample can emerge into the spectrometer. If the surface ionisation and the effective thickness of the surface layer are known for both specimen and standard, the ratio of emitted intensities can be calculated very simply in terms of the mass composition of the specimen.

To calculate the surface ionisation, ϕ (0), it is necessary to know the energy distribution of back-scattered electrons, for which several sets of experimental data now exist, and to assume that the electrons emerge at some mean angle to the surface. The accuracy of this approach is confirmed by direct measurements of the ϕ (0) by Castaing and by Henoc, and agrees well with Monte Carlo calculations of Bishop. Sets of ϕ (0) curves as a function of atomic number and overvoltage ratio are given.

The effective thickness of the surface layer is inversely proportional to the appropriate mass absorption coefficient. It is therefore necessary to check the accuracy of the "surface layer" method of correction on samples for which the mass absorption coefficients are known, such as for carbon K radiation in certain metallic carbides. The method is then used to establish mass absorption coefficients (for carbon K radiation) in cases where no data at present exists.

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13

FERGUSON, L. A. - Programed Microprobe Analysis With The Aid Of Multichannel Analyzer.

The use of the multichannel analyzer to increase the versatility of

the microprobe and to reduce the time required for qualitative analysis has been demonstrated.[1] In addition, because of its versatility, analytical techniques and data handling procedures may be adopted to improve precision and reliability of the results. For example, the solubility of Fe in a U specimen equilibrated at 550°C. has been determined at 89 ± 7ppm by a "chopped beam" method of analysis previously described.[2]

A multichannel analyzer (M.C.A.) has been programed with a microprobe in a manner that produces quantitative X-ray intensity measurements of up to 400 discrete points on the specimen. The analytical points may be accurately spaced along a line at intervals of 1μ or whatever distance is desired. The sample translation is accomplished by moving the electron beam (or a precision stage) through the use of a pulsed stepping motor. The motor is synchronized with a "live time" clock and the channel advance of the M.C.A. which is operated in the multiscaler mode. The rate of scan (or dwell time on the points) is variable. The system is designed to periodically sample a suitable matrix for background correction, if desired. The background is automatically subtracted from the sample measurement. Background measurements taken with the spectrometer set just above or below the peak of interest can also be subtracted. The result is a scan approaching theoretical precision which is corrected for background and pulse losses due to counting rate and from which accurate sample dimensions are readily determined. This system has particular application in the determination and display of diffusion gradients and phase homogeneity.

The digitized data produced are ideally suited to data processing techniques. A typical program is described as follows: The results of a scan across a continuous phase is produced on paper punch tape and sent to a computer where a simple program statistically eliminates, within preset confidence limits, the individuals which are not representative of the population. The points which are eliminated may be the result of small inclusions, cracks, or other surface defects. The results and their precision are then calculated for the remaining points. This precision is then compared to the theoretical precision as determined by standard counting statistics to provide a test for homogeneity. This technique has been applied to the analysis of elements in a uranium matrix where inhomogeneities or hidden inclusions just beneath the surface may jeopardize the results.

(Work performed under the auspices of the U.S. Atomic Energy Commission)

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[1] Birks, L. S., and Batl, A. P., Anal. Chem., 35, 778-82, (1963).

[2] Fergason, L. A., "A Method for Trace Analysis with an Electron Microprobe." A paper presented at the 14th Annual Conference of Applications of X-Ray Analysis, Denver Research Institute, Metallurgy Division, Denver, Colorado, August 25-27, 1965.

Mallinckrodt Chemical Works
Saint Charles, Missouri

GIBBS, G. V., and WHITE, E. W. - Structural and Chemical Effects On the AlKβ Emission Bands Studied by the Electron Microprobe.

The "chemical effect" on the x-ray emission spectra provides a rapid technique for the characterization of materials from the standpoint of predicting the valence, coordination number and short range structures of the constituents elements. However, to the person trying to obtain quantitative elemental analyses using long wavelength lines(wavelengths greater than about 2.5 Å), the "chemical effect" on X-ray spectra can be most annoying. Not only do many X-ray lines shift in wavelength but also changes in relative intensity and profile complicate the measurement of intensity ratios (standard versus unknown). Among the elements of low atomic number, the "chemical effect" is most pronounced for the K emission bands. For the third period elements, the Kβ lines are emission bands; however, for the second period elements the Kα line corresponds to the emission band making the effect a particularly important factor in quantitative chemical analyses of these elements.

This paper reports on part of an extensive program to study the "chemical effect" on the K emission bands of the light elements. For example, it was found in an earlier study that the position of the SiKβ line from silicates shifts in a predictable manner as a function of the mean Si-0 distance and the ratio of tetrahedrally coordinated Al to Si ions. Since the mean Si-0 distance is an indirect measure of the type of polymerization of the SiO_4 polyhedra in silicates, one can use the SiKβ shift to predict the tetrahedral linkage in unknown silicates and silicate glasses.

In the study of some forty Al-containing compounds - mostly oxides and silicates - the Alkβ peak position was found to vary over a range of about 0.009 A. For the case of Al coordinated by oxygen, the data fall into two separate groups characterized by four- and six-fold coordination. The mean separation between these groups is about 0.005 A giving a reliable method for predicting coordination numbers in unknown materials. The Al_2SiO_5 polymorph sillimanite, which has Al in both four- and six-fold coordination gives an AlKβ peak position in the region between the two groups. Initial evaluation of the data does not reveal any obvious dependence of shift on mean Al-O distance; however, the paucity of precise X-ray crystallographic data for the compounds studied makes the conclusion a bit tenuous. The peak shifts also appear to be dependent upon the kind of anion coordinating the Al. For example, fluorine and hydroxyl ions affect the peak differently than does the oxide ion.

Use of the electron microprobe in studies of line shifts has the obvious advantages of efficient excitation (one can hopefully study the structural role of many elements present in minor amounts) and

7

the ability to gain such information on the individual particles in the size range of a few microns is unsurpassed by any other technique. An additional advantage is that this technique is equally applicable to amorphous solids.

The AlKβ line recorded from the mineral sapphirine indicates that the Al ions are all six-fold coordinated by oxygen. Other examples will be presented demonstrating the use of this technique to predict the structural parameters of heretofore unsolved crystal structures.

Department of Geochemistry & Mineralogy
and the
Materials Research Laboratory
The Pennsylvania State University

15

GOLDSTEIN, J. I., and WOOD, F. - Experimental Procedure For Trace Determination With the Electron Probe.

Experimental procedures have been developed for trace analysis with the electron probe. These procedures are discussed and recommendations are given in order to allow the analyst to make accurate measurements in the 10 ppm range. Data have been obtained using these procedures for Ge in the metallic phases of meteorites (20-300 ppm).

It is well known that the minimum detectability limit (MDL) for an element of interest is proportional to (1) the peak intensity, (2) the peak to background ratio, and (3) the counting time. To improve the MDL for a given counting time, the sample current and high voltage should be increased as much as possible. The sample current can be increased to the point at which contamination build up and/or increased spot size becomes significant. Even though the peak intensity increases with the high voltage, the peak to background ratio does not necessarily increase. Therefore the high voltage setting can be best determined empirically. For our Ge work, we found the best operating conditions at 35 kv and 0.2 μA specimen current. For the maximum practical counting time of one hour (3600 sec.), the calculated MDL was 10 ppm at a 95% confidence level.

When pure element standards are used for trace analysis, very high count rates ($>$50,000 cps) are obtained. These high count rates cause severe peak energy shifts to develop in the detector. Therefore it was necessary to obtain a standard close in composition to the sample under investigation.

The amount of trace element C_x present is determined by the equation:

$$C_x = \left[(\bar{N}_x - \bar{N}_B)/(\bar{N}_c - \bar{N}_B) \right] C_A$$

where $\bar{N}_x$, $\bar{N}_B$, and $\bar{N}_c$ are the mean counts determined for the unknown, its background, and the calibration standard respectively, and C_A is the composition of the calibration standard. Since $(\bar{N}_x - \bar{N}_B)$ is very small in trace element analysis an accurate measurement of $\bar{N}_B$ is most important. The background may be determined in two ways: (1) moving the spectrometer off peak, or (2) measuring from standards identical to those under study except for the absence of the element desired. Since the background off peak varies with wavelength, an extrapolation must be made. However, this extrapolation is often too inaccurate for analysis in the 10 ppm range. In this study, background standards very close in composition to the sample were found to be necessary.

Probe stability is the key factor to a good analysis. We employed a current integrator to correct for short and long time drifts in the beam current. Electronic drift in the high voltage supply, amplifier pulse height voltage and detector voltage must of course be held to a minimum. These factors allowed us to obtain only an experimental MDL of 20 ppm, about twice that theoretically possible.

Goddard Space Flight Center
Greenbelt, Maryland

16

HEINRICH, K. F. J. and YAKOWITZ, H - Quantitative Electron Probe Microanalysis: Absorption Correction Uncertainty.

The purpose of this communication is to investigate the accuracy of proposed methods for the absorption correction in electron probe microanalysis. It contains the following sections.

1. A list and comparison of the experimental values for the absorption function $f(\chi)$.

2. A comparison of some proposed methods for calculation of the absorption function, with the experimental evidence.

3. Using as a working model the Philibert expression as modified by Duncumb and Shields, the effects of errors in the mass attenuation coefficient, the mean X-ray emergence angle, and the applied operating voltage on the function f( ); and, hence, on the analytical result, are given in a general equation. These effects are illustrated using as an example a 50 Al-50 Mg alloy.

The effects of input parameter errors are shown to be seriously increased as the value of f( ) decreases. The prevalent source of error is in most cases the mass attenuation coefficient uncertainty. An expression is given that permits selection of the operating voltage for any specific case so as to obtain a predetermined value for f( ). This equation shows that in analysis involving soft x-rays with an instrument having a low take-off angle, sufficiently high f( ) values cannot be obtained at reasonable operating voltages.

National Bureau of Standards
Institute for Materials Research
Washington, D. C.

17

KENWORTHY, A. L., and DRYER, H. T. - Electron Probe Determination of Nutrients in Plant Tissue.

Recent studies in plant nutrition and growth cycles have required the determination of elemental distribution within the plant tissue. Electron probe analysis because of its ability to determine the elements from boron through uranium in micron size volumes, is ideally suited for these investigations because of the inherent difficulties in this type of analysis. A variety of sample preparation techniques were investigated for plant tissue material to maintain the original cellular structure, to retain the nutrient distribution within these structures, and to provide a suitable microprobe sample.

The method of sample preparation, the analytical method, and the resultant data for a variety of plant tissue will be described.

Applied Research Laboratories, Inc.
Dearborn, Michigan

KEIL, KLAUS - Mineral Chemistry of Enstatite Chondrites.

Enstatite chondrites are a unique class of meterorites inasmuch as they were formed under higher reducing conditions than anyother group of meteorites. As a result of their formation in such an environment they exhibit unusual mineral assemblages including minerals not known from terrestrial rocks. At present there are 15 enstatite chondrites known to exist in the world's meteorite collections. The minerals constituting these 15 meteorites were analyzed quantitatively in great detail using electron microprobe techniques. In the course of this study the following minerals were analyzed: kamacite, α-NiFe; taenite, γ-NiFe; graphite, C; troilite, FeS; oldhamite*, CaS; daubreelite*, $FeCr_2S_4$; sphalerite, (Fe, Zn)S; complex isomorphous mineral series with NaCl-structure, Mg-Mn-Fe-Ca-Zn-Cr-S; enstatite, $MgSiO_3$; clinoenstatite, $MgSiO_3$; plagioclase, $NaAlSi_3O_8$-$CaAl_2Si_2O_8$-$KAlSi_3O_8$; quartz, SiO_2; tridymite, SiO_2; cristobalite, SiO_2; schreibersite*, $(Fe, Ni)_3P$; cohenite, Fe_3C; lawrencite*, $FeCl_2$; perryite*, $(Fe, Ni)_x(Si, P)_y$; and sinoite*, Si_2N_2O. A comparative study of the compositions of these minerals and their relative abundances, and of the bulk chemical composition and texture of the individual meteorites reveals the existence of two groups of enstatite chondrites, which differ not only in composition, but also in degree of recrystallization. The boundary between the two groups is, however, not very sharp. The apparent relationship between degree of recrystallization and composition of the meteorites is discussed and three models are suggested to account for this relationship. The most likely model seems to be that the enstatite chondrites were originally different in their bulk compositions (particularly in total iron and sulfur), while later recrystallization may have been the cause for the observed changes in the composition and abundance of certain minerals.

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*Minerals marked by asterisk do not occur in terrestrial rocks.

National Aeronautics & Space Administration, Space Sciences Division
Ames Research Center
Moffett Field, California

19

KIMOTO, S., and HASHIMOTO, H., and TADA, K. and MAGAI, T. - Quantitative Analysis of Light Elements with an Electron Probe X-Ray Microanalyzer.

As a result of the development of a detector and an analyzing crystal for the soft X-rays, the range of the elements detectable through an electron probe X-Ray microanalyzer has been extended to the elements lighter than sodium. As far as qualitative analysis of such light elements as carbon, nitrogen and oxygen is concerned, satisfactory results can be obtained.

As concerns a quantitaive analysis, however, many problems remain to be solved. One of them concerns the correction methods of measured values. Generally there are two correction methods in quantitative analysis: One is that the value is corrected with a calibration curve which is established by using several standard specimens and the other is to correct the value by calculation using the absorption coefficients.

For the determination of a concentration of carbon in a steel specimen, a straight calibration curve can be used over the range from 0 to 1%. But when measuring a specimen for which reference standard specimens are not available, the calculation is the only way of correction.

Results are presented and accuracy is discussed with regard to the absorption correction of carbon or oxygen in carbide specimens such as SiC, Fe_3C, Cr_7C_3, Cr_3C_2, and oxide, MgO, Al_2O_3, SiO_2, $CaCO_3$, Fe_3O_4, Fe_2O_3, etc.

The results of oxygen in MgO, Al_2O_3, SiO_2 and $CaCO_3$ show that there is a linear relation between the true values and corrected values with relative errors of less than 6%.

Japan Electron Optics Laboratory CO., Ltd
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20

LEWIS, ROBERT, RUDERMAN, W., and ROUBEROL, J. P. - Quantitative Studies of Various Analyzer Crystals for Use in Electron Beam Microanalyzers.

In the ideal case, it is desirable to select for any particular

application an x-ray analyzer crystal having the highest reflectivity and resolution. If crystals are to be compared, the history of each crystal specimen and a knowledge of its perfection are essential. A selected number of useful crystals have been studied in an electron beam microanalyzer to determine resolution and relative reflectivity. For each crystal, a measure of the perfection was obtained by measuring the crystal rocking curve with a double crystal X-ray spectrometer having an overall accuracy of $\pm$ 1.5 seconds. The reference crystal was a high quality KAP crystal with a full width at half maximum of two seconds.

Each crystal was then bent to a radius of 500 millimeters and used to analyze soft fluorescent X-rays in an electron beam microanalyzer. The resolution and relative signal-to-noise ratios for each crystal were determined under comparable experimental conditions. Selected crystals of ADP, PET, EDDT and quartz, with 2d spacings of 10.64, 8.75, 8.80, and 8.50 A respectively, were compared for phosphorus, calcium, and titanium characteristic radiation. Crystals of PET and EDDT of widely different crystal perfection, as evidenced by their rocking curves, were compared as analyzer crystals.

For the analysis of soft radiation beyond 25 A, only sterate monolayer films have hithertofore been available. Single crystals of OHM*, large enough to be used in a microanalyzer, have recently been grown and were compared with monolayer stearate films for the analysis of carbon, nitrogen, and oxygen characteristic radiation.

Acton Laboratories, Acton, Massachusetts;
Isomet Corporation, Palisades Park, N. J.;
C.A.M.E.C.A., Paris, France

21

LIFSHIN, E., and HANNEMAN, R. E. - <u>An Automated Method For The Collection and Analysis of Microbeam Probe Data</u>.

Quantitative applications of the electron microbeam probe frequently involve the evaluation of complex mathematical expressions and/or the analysis of large amounts of experimental data. This paper will describe both equipment for automatically collecting data and a computer system which contains a group of programs that can be run individually or in an arbitrary sequence to rapidly evaluate a number of practical microprobe problems. A teletype has been incorporated into the microprobe system for the purpose of both transmitting data and receiving computer output.

A specimen stage for a Cambridge Mark II instrument has been designed and built to accomodate a standard size 1 ¼" metallographic sample and accurately translate it on x and y directions by micrometer controls calibrated in micron units. The x translation which is perpendicular to the focusing circle of two spectrometers can be connected to either an electronically controlled stepping motor, which can be used to translate the sample under the electron beam in steps of 2 to 200 microns, or to a multiple speed motor to continuously translate the sample at speeds of 5 to 250 microns per minute.

When used in the stepping mode the number of data points to be taken can be pre-set by means of a counter which also provides a digital value of the step position. Data in digital form is also obtained from two x-ray detection channels and a specimen current meter at each point. This information is recorded on a punched paper tape by a device which converts parallel to serial output and inserts appropriate blocking characters. Following the recording of data from each point a signal is sent to the stepping motor controller to advance the sample to the next step and take data and so on until the scan is completed.

The computer program system consists of ten programs which are stored in a disc library. Information calculated by any single program can be made available to any other program. Included in the library are programs to:

1. Determine the transfer of control between programs.
2. Generate either theoretical calibration curves or calibration curves from standards.
3. Read in data on paper type input and convert to magnetic tape for subsequent manipulation.
4. Convert raw x-ray data into composition for any number of data points.
5. Perform a Matano analysis on diffusion data.
6. Calculate activation energies and frequency factors from diffusion data.
7. Calculate relative intensity generated from thin films as a function of thickness.

Versions of the system have been prepared for use with or without a teletype connection to the computer. When used with a teletype data can be read in either by a tape reader or by a typewriter. The choice of programs applicable to a given problem and the particular input data are automatically requested by the computer in form convenient for the operator. If teletype equipment is not used, standard methods of card reading and tape reading can be used. In either case, programs can easily be added to the library or existing programs can be modified to incorporate new theoretical methods. Examples of input and output will be presented.

General Electric Research & Development
Center
Schenectady, New York

22

LUBLIN, P., and SUTKOWSKI, W. J. - Electron Probe Techniques in the Analysis of Refractory Metal Coatings.*

The electron probe is ideally suited to the analysis of coatings on refractory metals and alloys. These coatings are normally about 50 microns thick and contain many narrow zones and small isolated regions of assorted intermetallic and oxide phases.

The probe techniques employed include beam scanning images for survey information on the distribution of elements in the coating; concentration profiles for the observation of concentration gradients and semi-quantitative analysis; and quantitative analysis for the identification of the structural phases present.

In quantitative analysis use was made of a modified version of Brown's[1] computer program. In order to reduce atomic number effects, standards such as disilicides of the various elements were used in addition to pure metals. Comparative calculations will illustrate the effectiveness of this method.

The substrate materials included in this program were columbium, molybdenum, tantalum, tungsten and their alloys. The coatings employed were silicides and modified silicides. The samples were examined in the as-coated, and as-oxidized conditions.

Sample preparation techniques will be discussed as well as the analytical results on the various systems. Structure identification by X-ray diffraction was used to supplement electron probe analysis.

* Supported by Air Force Materials Laboratory, Wright-Patterson AFB, Ohio

(1) J. D. Brown, "A Computer Program for Electron Probe Microanalysis", U. S. Bureau of Mines Publication TN 23.U7, No. 6648.

General Telephone & Electronics Lab, Inc.
Bayside, New York

23

MACRES, V. G., and PRESTON, O. - Electron Microprobe Analysis At Elevated Temperatures.

The principle characteristic of the electron microprobe analyzer is its

ability to obtain information from microscopic areas, thus providing additional means for correlating microscopic and macroscopic behavior. To date, the application of the microprobe to specimen analysis at other than ambient temperatures is virtually unknown. The ability to examine directly specimens at temperatures either above or below ambient is a logical extension of the microprobe method. Significant information relating to microscopic crystallographic and chemical changes during dynamic heating or cooling during microprobe analysis can be anticipated.

In this presentation, discussion will be directed to a hot stage design developed for use with the Model 400 Electron Microprobe Analyzer. Incorporated in this stage is a means for radiation and electron beam heating of the specimen as well as the necessary items for temperature measurement and cooling. In addition, a control unit provides for proportional temperature regulation of the specimen during analysis. Performance characteristics of the hot stage will be discussed and examples of its applications will be presented.

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24

MARTON, L. - Survey of Microanalysis - Interpolation and Extrapolation.

A review of the early history of the efforts to achieve a chemical analysis of very small areas of the surface of a specimen; besides the electron probe microanalyser, it includes other less successful attempts. Looking in the future, a few possible improvements are discussed together with expected applications.

National Bureau of Standards
Washington, D. C.

25

MEAD, C. W., and MROSE, M. E. - Solving Problems in Phosphate Mineralogy with the Electron Probe.

Qualitative and quantitative electron-probe analyses of nonconducting

minerals, in conjunction with single-crystal X-ray and powder diffraction data, have been used successfully to solve a number of problems in phosphate mineralogy.

By quantitative electron-probe analysis of two extremely rare minerals, type calcioferrite from Battenburg, Bavaria, and montgomeryite from Fairfield, Utah, inferred to be isostructural from powder patterns, their formulas have been established as $Ca_2Fe_2(PO_4)_3(OH).7H_2O$ and $Ca_2Al_2(PO_4)_3(OH).7H_2O$, respectively.

Fragments of type material of zincian rockbridgeite from Maxedo, Portugal, examined for homogeneity and composition by electron probe and then X-ray techniques on the same material, are shown to be a mixture of two minerals containing approximately equal amounts of zinc, zincian lipscombite is the major constitutent, and zincian rockbridgeite, the minor.

X-ray study of minute, colorless to pale-yellow hexagonal crystals, found sparingly on ore specimens from Butte, Montana, indicated the mineral to be a member of the plumbogummite group. Spectrometer traces, coupled with quantitative determinations of P and S, led to identification as hinsdalite, $PbAl_3(PO_4)(SO_4)(OH)_6$.

Single-crystal examination of a pale pink and a white fragment of attacolite from Westana, Sweden, yielded closely agreeing cell parameters but differing crystal symmetry. Qualitative electron probe analysis confirmed that both have similar composition, thus indicating that the white mineral is the monoclonic dimorph of orthorhombic attacolite. These data suggest that the monoclinic form is a new mineral species.

U. S. Geological Survey
Washington, D. C.

26

MENY, L., CHAMPIGNY, M., BELTRANDO, R., and SALAUN, P. - Solid State Diffusion in Zr-Cu and Zr-Ni Systems Study of the Obtained Intermetallic Compounds.

Solid state diffusion tests were made between metallic samples Zr-Cu and Zr-Ni. All tests were carried under the following experimental conditions: specimens were pressed under 425 psi, under secondary vacuum, the annealing time was 100 or 500 hours at different temperatures from 1200° to 1600°F. In each case, a parallel multilayered diffusion zone was formed.

The different intermetallic compounds were studied with metallographic methods (optic microscopy and microhardness), X-ray diffraction and Electron probe X-ray microanalysis.

X-ray microanalysis was carried out, first with CuKα (or NiKα) radiations, then with ZrKα and ZrLα, at different H.T. values (from 10 to 40 KV). It was then possible to determine the composition of the intermetallic compounds.

The six Zr Cu compounds were confirmed: Zr_2Cu, ZrCu, Zr_2Cu_3, Zr Cu_3, $ZrCu_4$ and $ZrCu_5$, as proposed in a recently published paper +, in which $ZrCu_5$ was mentioned for the first time, and compositions of $ZrCu_3$ and $ZrCu_4$ were proposed.

In the same way, six intermetallic compounds were found in the Zr-Ni system (instead of four as indicated by Hansen), with the same atomic compositions: Zr_2Ni, ZrNi, Zr_2Ni_3, $ZrNi_4$, $ZrNi_5$.

Comparison of these results suggests a binary diagram of the same type for both systems Zr-Cu and Zr-Ni.

+ G. Hillman - W. Hoffmann: "Dissusions messungen in system Kupfer-Zirkonium" Zeitschrifg fur Metallkunde 56, N° 5 mai 1965

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Paris, France

27

MOLL, SHELDON H. - Analytical Problems Associated with the Quantitative Determination of B, C, N and O in the Electron Probe.

The instrumental components required for the detection of the K emission characteristic x-ray lines of the light elements B, C, N and O in the electron probe have been well established. A thin window proportional detector, stearate crystal monochromator, vacuum path and electron trap, all required for spectrometers operating in the 20-100 A wavelength region, are now part of many operating microanalyzers.

On the other hand, very little experience has been established in the use of these analytical components in obtaining quantitative analyses for the light elements. Most of the analytical problems which arise are related to the carbon rich contamination spot.

It has been proposed that intensity measurements on carbon free specimens, which include the intensity produced by the slowly thickening carbon film, can be used to correct intensities obtained

on carbon rich samples such that the true intensity representing the sample carbon concentration can be obtained. It can be shown experimentally, however, that the rate of carbon contamination is itself a function of sample carbon content and this technique is invalid. A method of extrapolation is proposed which yields the true sample carbon counting rate.

The absorptive effect of the carbon rich contamination spot on $OK\alpha$ intensity is presented. It has also been shown that in addition to the presence of carbon in the contamination spot a small amount of oxygen is deposited which affects the analysis for low oxygen concentrations.

The specular reflection of the long wavelengths from the monochromating crystal and its effects in slowly increasing the background intensity is also discussed.

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Burlington, Massachusetts

28

MORRIS, W. G. - Crystal Orientation and Lattice Constants From Kossel Lines.

A generalized approach for determining crystal orientation as well as the lattice constants from Kossel patterns has been developed. The mathematical expressions are not difficult to obtain; the actual computations are best handled by a computer. Any conic appearing on a flat photographic film must fit an equation of the form $l_1x + l_2y + l_3z - \sin\theta\sqrt{x^2 + y^2 + z^2} = 0$. A rectangular coordinate system (x, y, z) is chosen with the x-ray source at the origin and the film at a distance D along the z axis. The direction cosines of the pole of the diffracting plane with the (x,y,z) axes are (l_1,l_2,l_3) respectively. The Bragg diffraction angle is θ. If a traveling microscope is used to measure the (x,y) coordinates of three or more points lying on a given conic, then l_1, l_2,l_3 and $\sin\theta$ for the diffracting plane can be calculated. If the wavelength λ is known, then the d-spacing of that plane can be calculated; $d = \lambda/2 \sin\theta$. If more than three points on a given conic are measured, a least squares fit can be applied to give the best values of the direction cosines and $\sin\theta$. A Fortran program has been written to perform this analysis. For a given pattern, all the conics are tabulated according to decreasing d-spacing. For cubic materials, the conics can then be indexed after calculating angles between pairs of poles and comparing with a standard table of interplanar angles.

A sterographic projection of a Kossel pattern corresponding to a particular crystal and wavelength is very useful in determining crystal orientation and identifying conics on a film. The process of calculating and plotting the circles manually is tedious, and recently Arrhenius[1] has adapted digital computation and plotting techniques to produce the stereographic projections for cubic systems. An extension of that technique to any crystal system has been developed utilizing the reciprocal lattice concept. Only in cubic systems does the vector $h\bar{a}_1 + k\bar{a}_2 + l\bar{a}_3$ have the same direction as the normal to the (hkl) plane. In reciprocal space, however, the vector $h\bar{a}_1^* + k\bar{a}_2^* + l\bar{a}_3^*$ always coincides with the normal to the (hkl) plane and has the additional characteristic that its length is $1/d_{hkl}$. The necessary transformations are conveniently represented in matrix form, and the actual computation and plotting is performed by a digital computer. The flexibility offered by this technique permits one to obtain the radii and center coordinates of all circles or sections of circles appearing on the sterographic projection and, if a x-y plotter is available, the complete plotted projection. This can be done for (1) any crystal by specifying the lattice constants $(a,b,c,\alpha,\beta,\gamma)$, (2) any specified wavelength or combinations of wavelengths, and (3) any specified (hkl) pole to be placed in the center of the projection.

The precise measurement of lattice parameters has previously been limited to cubic crystals. The procedure outlined by Gielen, et al, [2] for machine computation of suitable conic intersections has been extended to cover any crystal system. The reciprocal lattice is used in this development also, and all sensitive intersections of conics are tabulated. However, the dependence of the intersections on the lattice constants is complex even for the tetragonal case. In general, one needs as many independent intersections as there are lattice constants to be determined. A convergent iteration method is currently being investigated as an approach to determining lattice constants of tetragonal and orthorhombic lead oxide.

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1 G. Arrhenius, Fourth International Congress on X-ray Optics and Microanalysis, September 1965, to be published. Hermann, Paris.

2 P. Gielen, H. Yakowitz, D. Ganow, R. Ogilvie, J. Appl. Phys. 36, (1965) p. 773-782.

General Electric Research & Development Center
Schenectady, New York

MOUDY, LAVADA A., and LAAKSO, CARL W. - Orientation and Lattice Parameter Determination of Electronic Materials by X-Ray Divergent Beam Photography.

The back reflection X-ray Kossel line technique has been used in making lattice parameter measurements and in determining crystallographic orientations of gold and gold-aluminum intermetallics present in microelectronic circuit interconnections. The geometric relationships encountered in X-ray divergent beam diffraction have been treated by Lonsdale (Ref 1) and were used in the interpretation of the Kossel line patterns.

The patterns were obtained using a standard back reflection Kossel camera in an Applied Research Laboratory EMX Model Electron Microprobe. The electron beam was focused to a focal spot size of approximately one micron diameter which produced the point source of divergent X-rays, characteristic of the atom species within the crystal. Diffraction of the X-rays occurs from atomic planes in the bulk of the crystal which satisfy the Bragg condition. The back reflection patterns obtained in this manner were analyzed according to previously established methods,[2,3,4] and compared with constructed standard Kossel sterographic projections.

The techniques developed for obtaining highly resolved patterns are discussed. Metallurgical techniques used to synthesize the intermetallic compounds are also described. Since it is desirable to obtain patterns from flat "undistrubed" surfaces of known orientation, a method was developed which employs electron beam melting of the material on to a single crystal substrate. The substrate was then removed by etching resulting in a planar surface.

All Kossel patterns were obtained using a specimen to film distance of approximately two centimeters, excitation voltages up to 50 kv, and beam currents of the order of 0.1 microamperes. Exposures times varied from one to three minutes. It has been demonstrated that it is possible to obtain "true" Kossel line patterns of elements such as gold, and binary systems such as aluminum-gold. These patterns, along with standard electron microprobe analyses, give a quantitative measure of the chemical compostion and lattice parameters of a material.

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1 K. Lonsdale, Phil. Trans. Roy. Soc. (London) A240, 219 (1947)
2 P. Gielen, H. Yakowitz, D. Ganow, and R. Ogilvie, J. Appl. Phys. 36, 773 (1965)
3 R. E. Hanneman, R. Ogilvie, and A. Modrzejewski, J. Appl. Phys.
4 D. Wittry, Interpretation of Kossel Line Patterns, Applied Research Laboratory Report, Glendale, California, February 15, 1964

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30

NAGEL, D. J., and BIRKS, L. S. - Effects of Interstitial and

Substitutional Impurities on Diffusion in the Titanium-Niobium System.

A few atomic percent of interstitial impurities O_2 and N_2 and substitutional impurities V, Zr, Mo, Ta and Au have been added to pure Ti and pure Nb. One of these impure metals was then bonded to the other in the pure state. Diffusion effects after 24 hours at 1100°C were analyzed through use of anodizing and the electron probe. The effects of added impurities which were studied are: (1) Discontinuities in the concentration gradient at phase boundaries, (2) variation of the bulk chemical diffusion coefficient, and (3) changes in grain boundary diffusion.

At 1100°C, the chemical diffusion coefficient in the Ti-Nb system varies from 10^{-9} cm^2/sec at 10 a/O Nb to 10^{-12} cm^2/sec at 90 a/O Nb. The Ti penetrates about 90 microns into Nb in 24 hours but the Nb diffuses over 600 microns into Ti in the same length of time. This asymmetrical diffusion, similarity between Ti and Nb in atomic size, electronegativity and structure at 1100°C, and mutual solubility with several impurities made the TiNb system an attractive vehicle in which to study impurity effects. The impurity elements were chosen to allow interpretation of the impurity effects on the basis of relative size, valence, and electronegativity values.

U. S. Naval Research Laboratory
Washington, D. C.

31

NEALEY, C. C. - Electron Probe Microanalysis of the Gold-Aluminum Binary System Using Computer Correction Techniques.

Since the introduction and application of data processing equipment into the realm of theoretical corrections of microprobe quantitative analysis, the effort involved in processing the data has been greatly reduced. This has increased the quantity and, in our case, the quality of microanalysis, but often has served only to point to the lack of precision which is included in all phases of quantitative analysis. Time and again, the often-applied alternative approach of comparing identical or nearly identical standards to the unknown has proven to be the only sure way of analysis. One such probelm resulted in our construction and positive identification of all phases in the gold-aluminum binary system.

2

This paper describes the correction routine computer program which resulted from optimizing the theoretical calculations for the binary phases. Much of this correction program has been patterned after those of J. D. Brown, Bureau of Mines, J. W. Colby, National Lead Company of Ohio, and others, and generally appears to yield comparable results. The discussion will concentrate on the areas where modified empirical and theoretical methods obtained higher concentration accuracies for the gold-aluminum system.

Analysis was completed for the aluminum K and gold L and M lines. The results of calculating the concentrations with various pairs of lines will be presented.

Initial data was corrected for deadtime and drift with special care given to properly controlling and interpreting secondary electron current effects. Considerable error and difficulty in computation was eliminated by properly controlling this factor during sample testing. The other corrections, background, absorption, etc., were computed using various theoretical methods in an iterative routine. The resulting concentration differences will be shown.

Since the concentration of the samples was accurately known, the errors in the measurements are meaningful and yield good checks for the testing and corrections methods used. Therefore, the error results have been compared to functions of concentration, energy, and electron penetration. These curves will be presented for comparison with those of others for other systems.

Autonetics, 3370 Miraloma Avenue
Anaheim, California

NIKKEL, H. - Electron Probe Investigations of Metallurgical Problems Associated with Steel Research.

A variety of problems in our laboratory have been subjected to electron probe microanalysis.

The high contrast capability of specimen current images is demonstrated in the image data shown for several investigations. Structure is evident in the specimen current images taken of unetched steel samples and in a specimen with coarse pearlite, individual lamellae are clearly visible on the current image of a lightly etched sample. In multiphase inclusions, once the various phases are identified by microanalysis, it is possible to further assess the distribution of phases with reasonable accuracy merely by observing the degree of shading in the specimen current image. Fractional differences in atomic number are easily distinguished on the current image and phases often not obvious optically are clearly seen on the microprobe display tubes.

Some of the metallurgical investigations discussed include studies of intermetallic constituents observed in scale on (Cu, Ni)-bearing steel and some findings on the distribution of Cb in certain steels.

Several problems involving inclusion identification are presented from studies of seamless tubing samples, mechanically capped steel, and a grade of steel used in can lids.

In the processing of sheet products, thin films often remain on a surface to be plated or on the plated surface itself, deposited by cleaning or passivation treatments. These are not easily detected with the microprobe; but in testing various cleaning methods that are used on black plate, Si was detected at various levels on the unpolished material.

Whenever unpolished surfaces are examined, a high unreliability factor accompanies the data obtained and sometimes extraction replicas from the irregular surface provide means to deposit the material of interest in a better location and in a more concentrated amount than the way it occurs in situ. In extraction replicas from electrical sheet exhibiting high wattage losses, P was observed in the carbon films. These had been piled on a platinum foil for ease in probing.

In other investigations, the differences in the Fe content of wustite, magnetite, and hematite were readily observed which indicates that specific oxide phases can be identified in many cases. A final investigation reported deals with Mn distribution in line pipe steel based on point determinations in selected areas.

Youngstown Sheet and Tube Company
Youngstown, Ohio

33

ODETTE, G. R., and ZIEBOLD, T. O. - Count Rate Response of Gas Proportional Detectors.

Two peculiarities of the count rate response of gas proportional detectors used in electron beam microanalyzers have been observed. First, the observed count rate output is not related to the true incident count rate (photon current) in a simple way - the system dead time appears to be dependent on the incident count rate. Second, when the incident count rate is changed suddenly, a period of several minutes may elapse before the observed count rate reaches a steady value - that is, an "overshoot" or "undershoot" is evident in the observed count rate when the true incident photon current is suddenly increased or decreased. Both types of behavior, non-linearity and transient effects, are of sufficient magnitude to affect the accuracy of microprobe data unless properly taken into account.

This paper will report an investigation of these phenomena for several different detector geometries used in electron microanalyzers.

Massachusetts Institute of Technology
Cambridge, Massachusetts

34

OGILVIE, R. E., and PINELLA, A. - Empirical Method for the Analysis of Mixed Oxide Phases.

In 1964, Ziebold and Ogilvie described the "Empirical Method for Electron Microanalysis." This particular method has proved to be an extremely simple yet accurate technique. Because of its success in the analysis of metal alloy systems, where pure element standards are used as a reference, it was thought that this approach would be equally useful in the analysis of mixed oxides, in which the individual oxide phases are used as the reference standards.

In this paper the results of the analysis of the SiO_2-MgO-FeO ternary are described. It is proposed that the following empirical equation holds for the analysis of such mixed oxides as are present in the olivines and pyroxenes:

$$\frac{1-M_a}{M_a} = \bar{b}_{abc} \frac{1-C_a}{C_a} \qquad (1)$$

where M_a is the ratio of the intensity of the metal ion in the mixed oxide phase (i.e., olivine) to that intensity obtained from the metal ion in the pure oxide phase; $\bar{b}_{abc}$ is the average conversion parameter obtained from the weighted average of the binary conversion parameters, that is, for a multiphase system of i phases

$$\bar{b}_{abc} = \sum_{b}^{i} b_{ai} \, C_i \, / \, 1-C_A \qquad (2)$$

and C_i is the weight fraction of the oxide phase i.

It will also be shown that a single conversion parameter may be used for the olivine pseudo-binary $2MgO \cdot SiO_2$-$2FeO \cdot SiO_2$.

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Cambridge, Massachusetts

35

OLSEN, R. H. - Electron Microprobe Analysis of the Alpha and Beta Phases of 6Al-4V and 4Al - 3Mo - IV Titanium Alloys as a Function of Heat Treatment.

Electron microprobe analysis was done on the alpha and beta phases of Ti-6Al- 4V and Ti - 4Al - 3Mo - IV as a function of temperatures. Alloy samples were heat treated at temperatures ranging from 1100°F to 1900°F and water quenched to room temperature. The composition of the alpha and beta phases were then determined using the electron microprobe. The Ziebold - Ogilvie method was used to convert x-ray intensity data to concentration.

At low temperatures the beta phase was very small and there was dilution from the alpha, however, by extrapolating high temperature data to the lower temperatures good correlation with published data was found. The probe results were plotted as isothermal sections and the percent beta at temperature compared with lineal analysis and x-ray diffraction results.

The Boeing Company
Seattle, Washington

36

ONG, P. S. - A Combined Cold Plate and Secondary Electron Collector.

The well known phenomena of carbon contamination on a sample seriously

limits the ultimate use of the microprobe for analysis of light elements.

A "cold plate", cooled with nitrogen, has been designed to be inserted between the sample and the probe lens. The "cold plate" is electrically insulated from ground potential, thus serving as a collector for backscattered electrons.

In addition, a separate, very fine wire electrode is inserted between the plate and the sample. This electrode is also electrically insulated from ground potential. Because of its small dimension, the fine wire electrode collects only a small fraction of the backscattered electrons. By applying a positive potential of approximately 50 volts with respect to the sample, it will attract the low energy electrons, secondaries, emitted by the sample.

Thus, scanning pictures can be obtained which are very sensitive to surface chemistry and surface potential differences.

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37

OPENSHAW, I. K. - Modification of an Electron Probe X-Ray Microanalyser for the Analysis of the Elements in the Range Sodium to Boron.

The range of analysis of a commercial electron probe x-ray microanalyser has been extended to cover the elements between sodium and boron inclusive by the use of a combination of K.A.P. and Stearate crystals. Points of specific interest in the preparation and performance of the stearate crystals are mentioned.

When the window between the specimen chamber and the spectrometer is removed a large increase in the background noise is observed due to stray electrons and x-rays. This noise is greatly reduced by the design of a collimating system which is described.

The build up of contamination on the specimen surface has been observed and measured under various operating conditions. The effectiveness of a number of decontamination experiments are discussed.

Illustrations are given of simple light element analysis.

Scientific Apparatus Department
Associated Electrical Industries
Urmston, Manchester, England

38

RAPPERPORT, E. J. - Increased Spatial Resolution of the Electron Probe.

Ordinarily, the electron microprobe analyzer is used to gather quantitative information from volumes whose minimum projected surface dimensions are no smaller than the minimum diameter of the impinging electron beam -- one-half to one micron, approximately. In some instances, however, it is possible to increase the effective resolution of an electron beam by a factor of ten or more to provide composition information on a distance scale much finer than the actual electron beam diameter.

This may be done by examining in detail the interaction of a known (measured) incident electron spatial profile with an unknown (desired) impurity concentration profile to yield a known (measured) transmitted or back-scattered electron spatial profile. Analyzing the interaction of these three distributions as a superposition problem, one finds the profile of the observed back-scattered (or transmitted) current distribution, I (x), as the convolution of the impurity concentration profile, C (x), and the incident electron profile, B (x). Using x as a distance variable and m as an auxiliary distance variable, one may write:

$$I(x)=K \quad C(m)B(x-m)\,dm$$

The unscrambling of the impurity concentration profile from the other two is a mathematical problem involving the solution of the given integral equation relating the three profiles. The actual solution of this equation is most conveniently done with the aid of a computer.

A general description of the profile interactions, their mathematical relationships, and the solution for the impurity concentration profile is presented for the electron case, with an extension of the arguments to the x-ray case.

Ledgemont Laboratory
Kennecott Copper Corporation
Lexington, Massachusetts

39

ROBERTSON, M. M., and ESTILL, W. B. - Electron Probe and Electron Microscope Investigation of Identical Areas.

The importance of selected area investigation in optical, electron

microscope and electron probe studies is well-known. Optical photo-micrographs have been commonly used to help correlate electron probe and electron microscope data. However, it has been notably difficult to select an area for electron microscopy even after optical or electron probe studies have delineated small regions of interest. The present work involves a new technique called "identical area microscopy" which allows direct comparison of the results of optical, electron probe, and electron microscope studies of the <u>same</u> area. It is commonly known that a contamination film builds up on a specimen during electron probe studies to such an extent that it can actually influence the analysis during any but short duration studies. The present work describes a method of exploiting the contamination film deposited during scanning mode operation of the electron probe. The resulting film proves to be an excellent surface replica for electron microscope studies - hence, a method of doing "identical area microscopy". Examples of the methodology will be shown and the techniques and steps involved in the replication process, as well as possible extensions of the method, will be discussed.

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Albuquerque, New Mexico

*This work was supported by the United States Atomic Energy Commission.

40

RUCKLIDGE, J. - <u>A Computer Program for Processing Microprobe Data</u>.

A FORTRAN IV program has been written for the purpose of processing electron probe microanalytical data from minerals. The program is designed to produce a complete compositional analysis of any mineral, given intensity data from all the elements in the unknown sample (with the exception of oxygen) and comparitive data from the same elements in a series of standards. The concentrations of elements in the standards need not be similar to those in the unknown, though in the case of major elements this will usually be so.

Corrections are made for absorption, x-ray generation efficiency and fluorescence effects after the methods outlined by J. V. Smith (J. Geol. 1965). In the first place I_A/I_{100A} is calculated for the elements in the standards, where I_A/I_{100A} is the intensity of the element A in the standard referred to the intensity of pure element A. An apparent concentration is found for element A in the unknown by linear comparison, and a first approximation to the total composition is obtained. Any discrepency between the sum of the the concentrations and 100% is made up by assuming the rest to be oxygen. The x-ray yield of this first approximate composition is calculated and compared with the observed data. Adjustments are

made in successive iterations until the agreement between calculated and observed intensities for the unknown is 0.2% or better for each element. The data from a mineral containing ten elements (including oxygen) may be processed by the IBM 7094 in about 1.5 secs, and this usually involves about 5 iterations.

Results obtained through this method will be presented and discussed.

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41

SAFFIR, A. J., and OGILVIE, R. E. - Analysis of Oral Tissues by X-Ray Absorption with the Electron Microanalyzer.

One of the problems encountered in the analysis of biological tissue is its decomposition by the electron beam. In order to overcome this difficulty an X-ray absorption technique has been developed with which, by a suitable choice of X-ray targets, one is able to determine the mass per unit area of a particular element. The resolution obtained is determined by the size of the X-ray source produced in the target material.

Examples are given of scanning display - absorption analysis and absorption profiles which are related to a study of teeth.

Massachusetts Institute of Technology
Cambridge, Massachusetts

42

SHINODA, GUNJI, and KAWABE, HIDEAKI, and SHIRAI, TASUKU - Improvement of Resolving Power of EPMA by Specimen Current Method and Its Application to Metallurgical Problems.

It is usually believed that the specimen current of EPMA depends on

the mean atomic number of the specimen and that from this property quantitative analysis can be done by measuring the specimen current. The above statement is not always true; in copper-zinc system it was reported that the specimen current for γ-phase becomes much lower than that calculated from mean atomic number. Thus sometimes some kind of correction must be added to the value of the specimen current to obtain exact knowledge of compositions of the specimen. At the same time this correction term furnishes informations of physical properties of specimen and the specimen current method becomes a useful tool even in the field of solid electronics. For example, if we scan the electron beam on germanium specimen, the change of the specimen current corresponding to the defect of crystal structure will be observed.

Another point to be mentioned in specimen current method is its superior resolving power to that in the x-ray spectrometric method. The size of x-ray source is about 3 $\mu\phi$ for 1 $\mu\phi$ electron beam of 30 kV energy for copper specimen as theoretically and experimentally determined by Shimizu and Shinoda*. As for the specimen current, the main part of which is determined by the atomic number and therefore, possibly is a function of the depth of complete diffusion, the diameter of the specimen current beam may not be so large compared to the diameter of the electron beam. We have experienced this in the case of diffusion in titanium and silver system and some theoretical calculations were done. Also this method has been applied to the analysis of cored structures of copper alloys.

In a cast state of α-brass containing 30% zinc, two components, one corresponding to the suppressed liquidus and the other with varying compositions, were found and from their compositions determined by EPMA and x-ray diffractometer, the effect of cooling velocities on the mechanism of solidification will be discussed. As the temperature range of solidification of α-bronze containing few per cents of tin is much larger than that of α-brass, the results of line scanning analysis using specimen current method are somewhat different from those of α-brass.

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*R. Shimizu and G. Shinoda: Technol. Repts. Osaka Univ., 14,897 (1964).

43

SPENGLER, C. S., and STICKLER, R. - A Practical Method of Presentation of Microprobe Data and Its Application to the High-Temperature Corrosion of a Ni- and a Co-Base alloy.

In spite of advances in the techniques and in the sophistication of

data handling, the results obtained by electron probe microanalysis require considerable effort in interpretation. Instrument variables as well as specimen parameters must be taken into account. A relatively large number of individual specimen areas must be analyzed to arrive at information of statistical significance. In order to facilitate the interpretation, the analytical data need to be combined with data obtained from light and electron microscopy, and x-ray and electron diffraction studies.

Frequently, the test results have to be presented to persons not familiar with the fundamentals and techniques of electron beam microanalysis. The presentation must be understandable yet economical with regard to time and costs. Electron and x-ray scanning micrographs commonly used for this purpose, however, can often lead to misinterpretation, Therefore, one needs to eliminate distracting factors such as instrument electronic noise, interference effects, background intensities, and distortion, for the presentation of the scanning data.

Experiences has shown that a simplified schematic or pictorial presentation of the combined information from the various techniques of examination is more useful and eliminates the chances of misinterpretation. Information from many specimen areas can be combined in a single diagrammatic composite, which can contain all the pertinent characteristic chemical, crystallographic and microstructural details.

As an example of this method of presentation, results of a study on the high-temperature corrosion of a Ni-base and a Co-Ni-base alloy will be presented. Samples of these alloys were coated with a low melting salt mixture and heated in a SO_2-containing atmosphere. After testing, all specimens exhibited under the optical microscope typically a two-layer corrosion scale and an affected alloy region immediately beneath the scale. Several different phases were apparant finely dispersed in the affected alloy region as well as in the corrosion scale.

By electron probe point and scanning analyses the segregation and migration of the various major and minor alloying elements in addition to the distribution of sulfur could be revealed, while supplementary x-ray diffraction analysis was employed to identify the various phases formed. With the aid of a schematic composite, containing a large number of individual data and scanning micrographic results, the complicated corrosion mechanism could be described readily. It can be summarized as follows.

During an initial "incubation" period, attack initiated by nucleation and growth of Cr-rich sulfides up to 30 μm below the specimen surface. In these regions the matrix of the alloy becomes depleted in Cr. At a critical Cr-content the remaining Ni-rich alloy and the sulfides are oxidized. The oxides form the inner corrosion scale which reacts with the salt mixture to form the outer corrosion scale.

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SWANSON, N., and POWELL, C, J. - Excitation of Electrons from Soft X-Rays Levels in Al, Al_2O_3, and Be by 23 keV Electrons*.

The distribution of energy loss of 23 keV electrons transmitted through thin films of Al, Al_2O_3, and Be has been measured at zero scattering angle. Loss spectra were obtained for an energy loss range of 60 to 180 eV, corresponding to excitation of L-shell electrons in Al and Al_2O_3, and to K-shell electrons in Be. From these loss spectra estimates have been made of the oscillator strengths and cross sections for the soft X-Ray transitions involved. The films used were sufficiently thin (300-500 A) that no multiples of the characteristic energy loss peaks due to excitation of the valence electrons were detectable in the energy loss range of interest.

The Al and Be films were prepared by evaporation in vacuum, while Al_2O_3 films were prepared both by anodization and by heating Al films in air. For Al, an increase in the energy loss intensity at 72.6 $\pm$ 0.6 eV was identified as the L_{23} edge; further broad peaks were seen at 97 eV and $\approx$ 112 eV energy loss. These results agree well with peaks in soft X-ray absorption seen by Codling and by Sasaki using the continuum radiation from a synchrotron. For Be, the K edge was seen at 11.9$\pm$ 0.4 eV energy loss, with loss peaks occurring at 113.4 eV, 118.7 eV, 123.7 eV, and $\approx$ 140 eV. These values are also in good agreement with x-ray absorption data. Codling has obtained different soft x-ray absorption spectra for the crystalline and amorphous forms of Al_2O_3, and qualitatively similar differences have been observed in the energy loss spectra. The L_{23} edge of the anodized film was observed at 75.5 $\pm$ 0.7 eV, with loss peaks at 76.5 eV, 78.7 eV, 98 eV, and $\approx$ 123 eV. The Al_2O_3 film prepared by heating Al in air had its L_{23} edge at 76.8 $\pm$ 0.7 eV, with loss peaks at 78.7 eV, 83.8eV, 98 eV, and $\approx$ 123 eV. The electron energy loss and soft X-ray absorption results show a shift of peak maxima in the same direction in going from one film to the other, but disagree by 1-2 eV in the peak positions. Some of this discrepancy can be explained by smearing effects due to the poorer energy resolution in the energy loss measurements.

Oscillator strengths for these transitions in the electron energy loss mode may be estimated from the zero-angle energy loss spectrum by use of a recently developed comparison technique. Preliminary results for Al indicate that 6-7 of the L-shell electrons participate in the electron energy loss absorption in the region from the L_{23} edge to 130 eV. Estimates of oscillator strengths for soft X-ray transitions are presently being derived for the other materials. By making reasonable assumptions for the angular distribution of the inelastically scattered electrons, values for the total excitation cross sections can also be determined. The implications of these results to quantitative electron probe microanalysis will be discussed.

National Bureau of Standards
Washington, D. C.

*Work supported in part by the U. S. Atomic Energy Commission, Division of Biology and Medicine

45

TAYLOR, CHARLES M.- Preliminary Procedures Prior to Quantitative Microprobe Analysis of Mineralogical Specimens.

The basic procedures and methods of specimen preparation for quantitative electron microprobe analysis are defined. In addition, the requirements of polished surfaces are discussed.

The general sequence which should be followed for obtaining a quantitative analysis is as follows: (1) ore microscopy examination; (2) location and photomicrographic recording of areas and minerals to be analyzed including identification by color photomicrography; (3) determination of reference orientation of the polished section; (4) evaluation of vacuum-deposited conducting coating for beam instability and absorption effects; (5) evaluation of relative stability of mineral phases subjected to electron beam bombardment; (6) determination of semi-quantitative spectral analysis on each of the mineral phases to be analyzed; (7) programming of the final quantitative analysis procedure using data obtained in (4), (5) & (6), e.g., choice of reference standards, order of element analysis, selection of accelerating voltage and analyzing crystals.

Analysis examples using the outlined procedure is given showing the results at each stage and the manner in which these results were used to determine the final quantitative microprobe analysis. In particular, analysis results obtained from an iron-vanadium-oxide (Nolanite) will be presented. These results in conjunction with single and polycrystalline x-ray diffraction studies, density measurements, wet chemical analysis and wavelength shift studies of Fe and V-Lα spectral lines have provided the basis for radically redefining the crystal structure and chemical nature of this mineral.

Materials Analysis Company
Palo Alto, California

46

TOUSIMIS, A. J., BRADLEY, W. H., and VISSER, R. W. - Analysis for Elements from Solutions with the Electron Probe.

Samples of biological as well as non-biological importance containing Na^{+}, Mg^{++}, $SO_4^{=}$, Ca^{++}, Cl^{-}, Fe^{+++} and others in concentrations ranging from 1 ppm to 100 ppm can be prepared for electron probe microanalysis. Qualatitative as well as quantitative data can be obtained from such preparations. In the method developed for this analysis, differential centrifugation and standard dilution concentration procedures were used. Volumes analyzed were 0.2λ or less. Calcium, magnesium, and sodium in supernates of centrifuged samples obtained from different depths from lakes were analyzed. Similarly, extracellular (blood serum) as well as intracellular chlorine, sodium, calcium, and magnesium ions were measured. The data could be rendered quantitative by examination of similarly prepared standards.

Biodynamics Research Corporation, Inc.
Rockville, Maryland

TOUSIMIS, A. J., and HAGERTY, JON C. - Enzyme and Polysaccharide Localization in Biological Tissues with the Electron Probe.

During the last two decades, our knowledge of the morphology and chemical composition of cellular components has increased substantially as a result of the development of suitable methods for specimen preparation and physicochemical identification of isolated fractions. Preparation procedures for electron microscopy have rendered possible the appreciation of the resolving power of the modern electron microscope, while the results of biochemical reactions carried out on isolated cellular components can be utilized for the localization of macromolecular species such as proteins, carbohydrates, lipids, nucleic acids and others. Electron probe microanalyses of biological tissues (1,2) have been centered primarily in the localization and measurement of mineral or inorganic constituents inside as well as outside, the cell. However, identification of organic molecules *in situ* with the electron probe is possible only on tissue sections that have been specifically reacted with a suitable chemical identifiable with the electron probe. Some of the classical histochemical methods such as those employed for the localization by light or electron microscopy of alkaline and acid phosphatases (3,4) adenosine triphosphatase (5) and polysaccharides (6) can be used to localize the same with the electron probe. Materials examined with the electron probe for phosphatases include abdominal skin and small intestine of the frog, small intestine and liver of adult guinea pig and rat. For polysaccharides in addition to the small intestine of the above animals the epiphyseal plate of the tibia of young rats was also studied. Both frozen and embedded (in paraffin or methacrylates) tissue sections were treated for enzyme or polysaccharides, then finally coated with either carbon, aluminum or copper for examination with the electron probe. In addition, the staining reaction could be followed without attaining the required visible color or precipitate for light and electron microscopy respectively. The data can be rendered quantitative provided adequate controls and standards are examined under the same conditions.

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Biodynamics Research Corporation, Inc.
Rockville, Maryland

48

TROMBKA, J. I., and ADLER, I. - Analytic Method for a Non-Dispersive Analysis.

Presently, our laboratory is involved in developing an X-ray fluorescence unit with radioactive sources for use in extended lunar surface exploration missions. The induced characteristic X-rays are measured using proportional counters. A multi-channel pulse height analyzer is used to obtain the pulse height spectrum characteristic of the incident differential x-ray energy spectrum.

A linear least square pulse height analysis method has been developed to obtain the differential energy spectrum from the pulse height spectrum, characteristic of the incident differential x-ray energy spectrum. The technique allows for: compensation for instrumental gain shift, background subtraction, selection of the components present from a library containing most possible components, and for the calculation of statistical variance and covariance.

Qualitative analysis of a complex mixture can be obtained using this linear least square method, and presently some quantitative measurements can be made. Experimental measurements of pulse height spectra of a few rock types using a breadboard design instrument have been obtained. These spectra have been analyzed using the linear least square method, and results will be presented.

Goddard Space Flight Center
Greenbelt, Maryland

49

WITTRY, DAVID B. - The Voltage Dependence of Cathodoluminescence in Semiconductors.

Since the discovery of the electron-beam pumped laser, there has been increased interest in cathodoluminescence of semiconductors. Most of the experimental work which has been reported on cathodoluminescence has been concerned with the influence of carrier concentration, local defects, and impurity concentration on the efficiency of light production by electron bombardment. In these investigations, surface recombination has usually been neglected for several reasons, namely: (1) the intensities observed do not depend strongly on the surface treatment, (2) the effect of surface recombination has been assumed constant if the voltage and current of the electron beam are held constant, (3) the data becomes more difficult to interpret if surface recombination is included. The present work on the voltage dependence of cathodoluminescence indicates that none of these assump-

tions are valid. The influence of surface recombination on the cathodoluminescence intensity has been verified experimentally and theoretically for GaAs. The results indicate that surface recombination is not negligible and that the intensity for a given electron beam voltage depends both on the surface recombination velocity and the diffusion length of the minority carriers. Comparison of theory and experiment has been made using the Laplace transform of the excitation vs. depth neglecting absorption of the emitted radiation. The function which occurs in the equations for cathodoluminescence intensity is shown to be approximately the same as the absorption correction function $f(\chi)$ commonly used in electron probe microanalysis provided $\chi=1/\rho L$ where L is the diffusion length.

This work was supported by the Air Force Office of Scientific Research under Grant AF-AFOSR-76-66.

Department of Materials Science
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50

WOLF, RICHARD C., and MACRES, VICTOR G. - A Proposed Method For Calculating the Atomic Number Correction In Electron Microprobe Analysis.

The reduction of electron microprobe intensity data to accurate chemical concentrations often requires the application of a correction for effects of atomic number. A more rigorous approach to the electron diffusion model based on the electron deceleration theory of Bethe has been formulated (modified diffusion model) to determine effects of atomic number in multi-component systems. The model includes all variables on which atomic number effects are dependent, including (1) atomic number differences, (2) Z/A ratios, (3) accelerating voltage, (4) critical excitation voltage and (5) electron incident angle. In addition, the model may be used on multi-component systems and allows the complete separation of electron backscattering and mass penetration effects inherent in atomic number effects.

Direct application of the modified diffusion model in determining atomic number effects requires a very large number of calculations and numerical integrations. Even with the use of computer techniques this becomes time consuming and expensive. Therefore, a series of generalized empirical equations have been determined from a large number of results calculated by direct application of the

modified diffusion model. These empirical equations allow routine determinations of electron backscattering, mass penetration and total atomic number effects to be performed rapidly on any multi-element system. The equations also make possible a simplified tabulation of the atomic number correction as a function of several easily determined variables. A tabulation of this type provides an atomic number correction which is usable from a practical viewpoint for routine determinations but which is based on a rigorously defined model.

Examples of application of this procedure for correction of atomic number effects on several selected alloys of known composition will be presented. Comparisons with results obtained using other proposed procedures for correction of atomic number effects will also be presented.

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51

YAKOWITZ, HARVEY - Contrast of Transmission Kossel Photographs.

The photographic contrast of transmission Kossel patterns is examined in terms of the voltage and thickness variables since other parameters in the contrast equation generally cannot be controlled by the investigator; they are fixed functions of the material. It is shown that there is no single thickness yielding maximum contrast. However, manipulation of the contrast equation yields an approximation to the thickness and operating voltage relationship giving Kossel transmission photographs of nearly optimum contrast. Methods for calculating this relationship for any crystal-radiation combination are described. It is assumed throughout that the crystal is not completely free of imperfections; however, neither is the crystal assumed to be completely mosaic.

Institute for Materials Research
National Bureau of Standards
Washington, D. C.

52

ZEITZ, L. and ANDERSEN, C. A. - A Study of the Accuracy of the

Determination of Zinc Content in Rat Prostate Sections by X-Ray Microprobe Analysis.

Studies involving the use of the electron microprobe x-ray technique in obtaining localized zinc analyses in the rat prostate have been previously reported(1). These analyses were carried out on 7μ thick, freeze-microtomed rat prostatic tissues. The Zn-Lα line was used in quantitative determinations, with accelerating potential of 10KV and sample currents of 0.035 A. A statistical study of all the determinations suggests a uniform zinc distribution in the analyzed ventral sections and non-uniformity in the lateral and dorsal sections. The uniformity of zinc distribution is the vetral lobe presented a method for assessing the accuracy of the x-ray microprobe determinations in vetral sections. This was accomplished by a comparison of zinc determinations obtained with the x-ray microprobe to that obtained on the adjacent serial section by means of a nondispersive x-ray emission technique(2). For 32 microprobe analyses on a ventral section, we obtained 0.007±.003%, where these values represent the weight percent of the average ± 95% confidence limits in weight percent, and for the nondispersive analysis of the entire serial section 0.015% with the confidence limits uncertain due to interelement interferences which are possible with this method.

Subsequent to the study outlined above, a dispersive-nondispersive x-ray emission technique was developed which eliminated the problem of interelement interferences(3), and allowed for a more reliable determination of the zinc content of the entire serial section. The study outlined above was repeated using 5KV electron accelerating potential in quatitative zinc analysis with the x-ray microprobe, and a dispersive-non-dispersive method in determining the average zinc content in the serial section. These latest results give 0.015 ±.003% for the average and ±95% confidence limits for 20 microprobe analyses and a weight percent of 0.02% for the adjacent serial section based on a single determination with the dispersive-nondispersive technique, with an estimated ± 95% confidence limit of ±0.01% based upon errors found with standards of approximately equal dry mass and zinc content.

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(1) Zeitz, L. and Anderson, C. A., IV Congres International-L'Optique des Rayons X et la Microanalyse, Orsay, France,(1965)
(2) Hall, T., Science, 134, 449 (1961).
(3) Zeitz, L., Anal. Bioch. 14, (1966).

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ZIEBOLD, THOMAS O. - Empirical Calibrations for Metal Oxides and Carbides.

Analysis of metal oxides and carbides with the electron beam microanalyzer has been undertaken for the purpose of extending the empirical method for treating calibration data. By this method, experimentally determined conversion parameters are evaluated from the equations

$$(1-K_A)/K_A=\bar{a}_{A(N)}(1-C_A)/C_A$$

and

$$\bar{a}_{A(N)}=(a_{AB}C_B+a_{AC}C_C+\ldots)/(C_B+C_C+\ldots)$$

in which K_A is the relative x-ray intensity emitted by element A from a mixture fo elements A, B, C, ... (the x-ray intensity is taken relative to that emitted from pure element A), C_A, C_B, C_C,... are the weight fractions of elements in the mixture, and a_{AB}, a_{AC}, ... are the desired conversion parameters.

Several binary and ternary compounds in the systems uranium-zirconium-oxygen and uranium-niobium-carbon have been analyzed with an Acton Laboratories microanalyzer. This paper will report on the accuracy of the empirical method as applied to these data. Two aspects are considered: (1) the applicability of the method to ternary systems in addition to those reported previously in the literature, and (2) the applicability of the method to analyses for the light elements carbon and oxygen.

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